

boundary between them. This is obviously not the case for the conjunction of layers of tungsten and the mixture of tungsten with tungsten carbide which is characteristic of this patent.

Please replace the paragraph beginning at page 8, line 11 with the following rewritten paragraph:

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By using the proposed invention and also the described new method of coating deposition, one can also obtain multilayer coatings with alternating layers of tungsten and layers containing tungsten carbides alloyed with fluorine and possibly with fluorocarbon compositions, including mixtures of these carbides with each other and with tungsten or carbon. The ratio of thicknesses of the alternating layers ranges from 1:1 to 1:5.

Please replace the paragraph beginning at page 8, line 18 with the following rewritten paragraph:

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The construction material itself, with a bilaminar or multilayer coating deposited in accordance with the proposed method, is also an object of this invention.

Please replace the paragraph beginning at page 9, line 1 with the following rewritten paragraph:

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The examples given illustrate the production of complex coatings in which the layer of coating containing this or that tungsten carbide or mixtures of the carbides with each other and with tungsten and carbon is superimposed on a tungsten layer previously deposited on the substrate. The examples cover bilaminar coatings (internal layer of tungsten and external layer containing one or more tungsten carbides), and multilayer coatings with alternating layers of tungsten and layers containing tungsten carbides.

Please replace the paragraph beginning at page 9, line 9 with the following rewritten paragraph:

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The construction material on which the composite coating is deposited (or its external layer relative to the coating, in the case of bimetal) contains one of the following base materials: hard alloys (cemented carbide), ceramics such as silicon carbide, silicon nitride, aluminium oxide, zirconium oxide, carbon-carbon composition materials etc., several iron-containing alloys such as iron, carbon steels, stainless steels, tool and high-speed steels and cast iron, or other materials from the following list: copper, silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, silicon, tantalum, niobium, vanadium, tungsten, molybdenum, carbon, nitrogen, boron, their alloys, compounds and mixtures, and also titanium alloys. The construction material or its outer layer adjacent to the coating should preferably consist of alloys with a nickel content exceeding 25 wt% e.g. Invar, Nichrome, Monel etc.

Please replace the paragraph beginning at page 9, line 21 with the following rewritten paragraph:

In the case of deposition onto chemically active materials such as iron, carbon steels, stainless steels, tool and high-speed steels, cast iron, titanium alloys and hard alloys (cemented carbide) containing titanium, it is preferable to deposit intermediate coatings containing materials chemically resistant to hydrogen fluoride, from the following list: copper, silver, gold, cobalt, nickel, rhodium, rhenium, platinum, iridium, tantalum, molybdenum, niobium, vanadium and boron. An intermediate coating of thickness 0.5-20 µm is deposited by electrochemical or chemical deposition from aqueous solutions, melt electrolysis, chemical or physical vapour deposition (e.g. by means of magnetron spraying) or by other methods.



Please replace the paragraph beginning at page 10, line 14 with the following rewritten paragraph:

The substrates, degreased and free of contaminations, are put inside a direct-flow chemical reactor with an electric heater. The chemical reactor is evacuated by means of a roughing pump with a liquid nitrogen freezing trap up to maximum vacuum, after which hydrogen or argon is supplied to the reactor. The reactor with the items in it is then heated to the required temperature, which is maintained for 0.5-1 hours. After this, the required hydrogen flow rate and total pressure in the reactor are set. The required flow rate of tungsten hexafluoride, heated beforehand to 30°C, is then set. After the retention of the items in the set conditions for the time necessary for the application of the internal tungsten layer, the required total pressure is set and a certain flow rate of the carbon-containing gas (e.g. propane), previously heated to the required temperature, into the reaction mixture is set. A multilayer composition coating is obtained by repeating the operation. After that, the supply of gas is terminated and the substrates are kept at constant temperature for 0.5-1 hours. After this stage, the temperature of the reactor is decreased to room temperature with hydrogen or argon being continuously supplied. The supply of hydrogen or argon is then terminated, the reactor is evacuated to maximum vacuum, and air is then admitted to it. The substrates with composite coatings are then removed from the reactor. Specific examples of the described method of deposition of a composite coating are described below. The tests for hardness and for determining the phase composition of the coating were carried out in the following manner.

Please replace the paragraph beginning at page 11, line 6 with the following rewritten paragraph:

Hardness tests were conducted using a PMT-3 instrument. Samples made from steel or hard alloys (cemented carbide) with the composite coating applied were cut across. The cut was then ground with emery cloth and polished with diamond paste to maximum smoothness. The microhardness of the coatings was determined by pressing the pyramid-shaped diamond micro-

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indenter of the PMT-3 instrument into the middle of the external or internal layer of the composite coating at the polished cross-cut of the sample. The results were averaged over 7-10 measurements. It was determined from them that the microhardness of the internal tungsten layer was 350-600 kG/mm², the microhardness of tungsten monocarbide (WC) was 1900 kG/mm², the microhardness of tungsten semicarbide (W2C) was 3000 kG/mm² and the microhardness of tungsten subcarbide W3C was 3100 kG/mm². The new tungsten subcarbide W12C possesses the greatest microhardness – 3500 kG/mm². Mixtures of tungsten carbides have intermediate hardness values.

Please replace the paragraph beginning at page 11, line 20 with the following rewritten paragraph:

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Multilayer coatings possessed medium hardness. In this case, the force on the diamond pyramid was selected so that the imprint extended into not less than four layers of the multilayer coating. These hardness measurements were also repeated 7-10 times.

Please replace the paragraph beginning at page 13, line 25 with the following rewritten paragraph:



A sample made from hard alloy (cemented carbide) VK-10 is retained in the reaction chamber at temperature 650°C in a medium of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.08 for 1 min and then in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.08 and a ratio of C₃H₈ to H₂ equal to 0.95 for 80 min; the C₃H₈ is thermally activated beforehand at 730°C and the reaction mixture pressure is 8.8°kPa.

Please replace the paragraph beginning at page 14, line 1 with the following rewritten paragraph:



The construction material thus obtained with hard alloy (cemented carbide) VK-10 as the base material has a composite coating with an internal tungsten (W) layer of thickness 0.7 µm and an

By Dura

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external layer (mixture of W_2C and WC) of thickness 32 μm . The microhardness of the coating is 2800 kG/mm².

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Please replace the paragraph beginning at page 19, line 4 with the following rewritten

paragraph:

A sample made from hard alloy (cemented carbide) VK6 is retained in the reaction chamber at temperature 620°C (a) in a mixture of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.08 for 2 min and then (b) in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.08 and a ratio of C₃H₈ to H₂ equal to 1.5 for 16 min; the C₃H₈ is thermally activated beforehand at 750°C and the reaction mixture pressure is 5.2 kPa. Operations (a) and (b) are repeated four times in succession. The fluorine content in the multilayer coating is 9·10⁻³ wt%.

Please replace the paragraph beginning at page 19, line 12 with the following rewritten paragraph:

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The construction material thus obtained with hard alloy (cemented carbide) VK6 as the base material has a composite coating with four alternating layers of W with thickness 3.0 μ m and of WC with thickness 7.0 μ m at a ratio of thicknesses 1:2.3 and total thickness of the composite coating 40 μ m. The average microhardness of the coating is 1320 kG/mm².

Please replace the paragraph beginning at page 19, line 20 with the following rewritten paragraph:

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A sample made from hard alloy (cemented carbide) VK10 is retained in the reaction chamber at temperature 650°C (a) in a mixture of tungsten hexafluoride (WF₆) and hydrogen (H₂) at ratio 0.08 for 1 min and then (b) in a medium of WF₆, H₂ and propane (C₃H₈) at a ratio of WF₆ to H₂ equal to 0.08 and a ratio of C₃H₈ to H₂ equal to 0.95 for 80 min; the C₃H₈ is thermally activated beforehand at 730°C and the reaction mixture pressure is 8.8 kPa. Operations (a) and (b) are repeated four times in succession.

Please replace the paragraph beginning at page 19, line 27 with the following rewritten paragraph:

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The construction material thus obtained with hard alloy (cemented carbide) VK10 as the base material has a composite coating with four alternating layers of W with thickness 0.7 μ m and of a mixture of WC and W₂C with thickness 32 μ m at a ratio of thicknesses 1:45.7 and total thickness of the composite coating 130.8 μ m. The average microhardness of the coating is 2200 kG/mm².

Please replace the paragraph beginning at page 24, line 30 with the following rewritten paragraph:

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The invention can be used for strengthening tools made from steel, hard alloy (cemented carbide) or diamond which are used for processing materials by means of cutting or pressing. The latter is the most promising field for applications of the proposed technology due to the absence of competing coating technologies applicable to the manufacture of press tools of complex shape for drawing wires and tubes and for extruding profile sections from aluminium, copper, steel and other metals and alloys. The carbon-tungsten coatings referred to can be deposited on tools and casting moulds used for moulding items from plastics, silicate masses and other abrasive mixtures.

IN THE CLAIMS:

Please amend claims 33, 67-70, 72, 76, and 81 as follows:

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33. (Twice Amended) Process in accordance with claim 31, characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys (cemented carbide) containing titanium, a coating is applied to them consisting of materials